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In re Patent Application of

ROHR

Serial No. 09/955,297

Filed: September 19, 2001

For: PHOTOVOLTAIC DEVICE

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Group:

Examiner:

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January 16, 2002

Assistant Commissioner for Patents
Washington, DC 20231

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Sir:

It is respectfully requested that this application be given the benefit of the foreign filing date under the provisions of 35 U.S.C. §119 of the following, a certified copy of which is submitted herewith:

Application No.	Country of Origin	Filed
0118150.2	United Kingdom	25 July 2001

Respectfully submitted,

NIXON & VANDERHYE P.C.

By: ____________________
Stanley C. Spooner
Reg. No. 27,393

SCS:kmm
1100 North Glebe Road, 8th Floor
Arlington, VA 22201-4714
Telephone: (703) 816-4000
Facsimile: (703) 816-4100

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26JUL01 E648027-3 D02246
P01/7700 0.00-0118150.2

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Imperial College of Science, Technology and Medicine
Sherfield Building
Exhibition Road
London
SW7 2AZ
United Kingdom

Patents ADP number *(if you know it)* — 0CL 03345 2001

If the applicant is a corporate body, give the country/state of its incorporation — United Kingdom

4. Title of the invention — Thermophotovoltaic Device

5. Name of your agent *(if you have one)* — D Young & Co

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

21 New Fetter Lane
London
EC4A 1DA

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6. If you are declaring priority from one or more earlier patent applications, give the country and date of filing of the or each of these earlier applications and *(if you know it)* the or each application number

	Country	Priority application number *(if you know it)*	Date of filing *(day/month/year)*
1st			
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and filing date of the earlier application

Number of earlier application	Date of filing (day/month/year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d))*		Yes
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11. I/We request the grant of a Patent on the basis of this application.

Signature | Date

D YOUNG & CO | 25 Jul 2001

Agents for the Applicants

12. Name and daytime telephone number of person to contact in the United Kingdom | Nigel Robinson | 023 8071 9500

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Thermophotovoltaic Device

This invention relates to an improved photovoltaic device/cell for the conversion of heat radiation into electricity.

Thermophotovoltaics (TPV) is the use of photovoltaic (PV) cells to convert heat radiation, e.g. from the combustion of fossil fuels or biomass, into electricity. The energy spectrum is often reshaped using selective emitters which absorb the heat radiation and re-emit in a narrow band. The re-emitted radiation may be efficiently converted to electric power using a PV cell of appropriate low band-gap. Higher PV cell efficiencies can be achieved by introducing multi-quantum-wells (MQW) into the intrinsic region of a p-i-n diode if the gain in short-circuit current exceeds the loss in open-circuit voltage [K.W.J. Barnham and G. Duggan, J. Appl. Phys. 67, 3490 (1990). K. Barnham et al., Applied Surface Science 113/114, 722 (1997). K. Barnham, International Patent WO 93/08606 and U.S. Patent 5,496,415 (1993)]. A Quantum Well Cell (QWC) in the quaternary system InGaAsP lattice-matched to InP substrates is a promising candidate for TPV applications as the effective band-gap can be tuned, out to about 1.65 μm ($In_{0.53}Ga_{0.47}As$), without introducing strain, by varying the well depth and width, to match a given spectrum. The enhancement in output voltage of a QWC is a major advantage for TPV applications [P. Griffin et al., Solar Energy Materials and Solar Cells 50, 213 (1998). C. Rohr et al., in Thermophotovoltaic Generation of Electricity: Fourth NREL Conf., Vol.460 of AIP Conf. Proc. (American Institute of Physics, Woodbury, New York, 1999), pp.83-92].

There is considerable interest in extending the absorption to longer wavelengths for higher overall system efficiencies with lower temperature sources; and lower temperature fossil sources have also lower levels of pollution. Appropriate and inexpensive substrates of the required lattice constant and band-gap are not available, so the lower band-gap material is often strained to the substrate, introducing dislocations which increase non-radiative recombination. Freundlich et al. have proposed strained quantum well devices [U.S. Patent 5,851,310 (1998), U.S. Patent 6,150,604 (2000)], but these can only incorporate a restricted number of wells without creating dislocations. Freundlich proposes limiting the number of wells to a maximum of 20, which will not produce sufficient absorption for efficient generation however. In a MQW system, these dislocations can be avoided by strain-balancing

the layers; alternating barriers and wells have bigger and smaller lattice-constants, but on average are lattice-matched to the substrate [N.J. Ekins-Daukes et al., Appl.Phys.Lett.75, 4195 (1999)]. The aim of strain-balancing techniques is to reduce the average or effective stress to zero by balancing the forces of tensile and compressively strained layers and thereby avoiding the formation of misfit dislocations.

Viewed from one aspect the invention provides a photovoltaic device having a multiple quantum well portion with alternating layers under tensile and compressive strain with respect to surrounding material such that the average stress in the quantum well portion is substantially zero.

With this concept one can extend the absorption threshold to longer wavelength without introducing dislocations.

With a strain-balanced multi-quantum-well stack in the intrinsic region of a two-terminal photovoltaic device the absorption threshold can be extended to longer wavelengths. In particular, with high bandgap barriers the dark current can be reduced at the same time, and hence the conversion efficiency is increased significantly.

What is needed to achieve higher conversion efficiencies is an improved voltage performance, which means a lower dark current. This is provided by the higher barriers which are also necessary to balance the strain.

A photovoltaic cell to convert low energy photons is described, consisting of a p-i-n diode with a strain-balanced multi-quantum-well system incorporated in the intrinsic region. The bandgap of the quantum wells is lower than that of the lattice-matched material, while the barriers have a much higher bandgap. The high band-gap barriers reduce the dark current. Hence the absorption can be extended to longer wavelengths, while maintaining a low dark current. This leads to greatly improved conversion efficiencies, particularly for low energy photons from low temperature sources. This can be achieved by strain-balancing the quantum wells and barriers, where each individual layer is below the critical thickness and the strain is compensated by quantum wells and barriers being strained in opposite directions. The strain is compensated by choosing the material compositions and thicknesses of the layers in such a

way that the average stress is zero, taking into account the elastic properties of the materials. Thereby the creation of misfit dislocations, which are detrimental to the dark current and hence to the cell conversion efficiency, can be avoided. The number of quantum wells that can be incorporated is therefore not limited by the build-up of strain, but only by the size of the i-region, and is typically 30-60. The width of the i-region is limited by the electric field that needs to be maintained across it.

The absorption can be further extended to longer wavelengths by introducing a strain-relaxed layer (virtual substrate) between the substrate and the active cell. The device is then grown on this virtual substrate and the layers are strain-balanced with respect to the new lattice constant. This allows one to effectively move to a specific lattice constant which is associated with a desired band gap for the lattice matched and strain-balanced materials. This is of particular interest for thermophotovoltaic applications with lower temperature sources, as one can extend the absorption towards the required long wavelengths.

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

FIG. 1 is a bandgap diagram of a strain-balanced quantum well cell. The p- and n-regions are made of material that is lattice-matched to the InP substrate, e.g. $In_{0.53}Ga_{0.47}As$ or InP. The quantum wells are made of $In_xGa_{1-x}As$ with $x > 0.53$, and the barrier of $In_xGa_{1-x}As$ with $x < 0.53$, GaInP or InGaAsP.

FIG. 2 is a schematic drawing of a strain-compensated quantum well cell where the width indicates the lattice parameter of the material when unstrained.

FIG. 3 is a graph of dark current densities of a strain-balanced quantum well cell (as depicted in Figure 2 but with 30 quantum wells) compared with bulk GaSb of similar effective bandgap (see Figure 4) and lattice-matched bulk InGaAs.

FIG. 4 is a graph of modelled internal quantum efficiency (with back-surface reflector) of a strain-balanced quantum well cell (as depicted in Figure 2 but with 30 quantum wells) compared with bulk GaSb and lattice-matched bulk InGaAs.

FIG. 5 is a graph of modelled internal quantum efficiency (with back-surface reflector) of a strain-balanced quantum well cell optimised for a Holmia emitter (not to scale).

FIG. 6 is a graph of the dark current of an AlGaAs/GaAs quantum well cell, where the data (dots) is fitted (black line). The modelled dark current density for a QWC with a higher band-gap barrier (grey line) is reduced.

As an example for a strain-compensated QWC, we consider a 30 well $In_{0.62}Ga_{0.38}As/In_{0.47}Ga_{0.53}As$ (InP) QWC, grown by MOVPE, whose sample description is given in Table I.

TABLE I: Sample description of a strain-compensated quantum well cell.

Layers	**Thickness (Å)**	**Material**	**Function**	**Doping**	**Conc. (cm^{-3})**
1	1000	$In_{0.53}Ga_{0.47}As$	Cap	p	1E+19
1	7000	InP	Emitter	p	2E+18
30	120	$In_{0.45}Ga_{0.55}As$	Barrier	i	
30	120	$In_{0.62}Ga_{0.38}As$	Well	i	
1	120	$In_{0.47}Ga_{0.53}As$	Barrier	i	
1	5000	InP	Base	n	1E+18
		InP	Substrate	n	

In FIG. 2 the strain-balancing conditions are shown, where the average lattice-constant of wells and barriers is roughly the same as the InP substrate. FIG. 1 shows a schematic diagram of the energy band-gaps of this kind of structure. This specific sample was not designed for TPV applications; the p-region, for example, is far too thick. It does not quite fulfil the ideal strain-balanced conditions, but close enough to avoid strain relaxation as is evident by the low dark current of the device (see FIG. 3). In fact, the dark current density is even lower than in a very good lattice-matched bulk InGaAs/InP cell [N.S. Fatemi et al., in Proc. 26th IEEE PV specialists conf. (IEEE, USA, 1997), pp.799-804] as shown in FIG. 3. In FIG. 4 we show the spectral response (SR) (=external quantum efficiency) data of the strain-balanced QWC at zero bias. The effective band-gap, resulting from the material composition and the confinement, is about 1.77 μm, which is well beyond the band-edge of lattice-matched InGaAs. Hence the strain-balanced approach has enabled the absorption threshold to be extended out to 1.77 μm while retaining a dark current more appropriate to a cell with a band-edge of less than 1.65 μm. The band-edge of the strain-balanced QWC is similar to that of a GaSb cell, but it has a lower dark current (see FIG. 3). Strain-balanced QWCs in

InGaP/InGaAs on GaAs have demonstrated dark currents comparable to homogenous GaAs cells [N.J. Ekins-Daukes et al., Appl.Phys.Lett.75, 4195 (1999)]. We have shown (see FIG. 3) that, if anything, $In_xGa_{1-x}As/In_zGa_{1-z}As$ (InP) cells with absorption edges out to 1.77 μm have lower dark currents than bulk InGaAs cells. To obtain even lower dark currents, we need a higher band-gap in the barriers. We can achieve that by using a different material for the barrier, such as $In_xGa_{1-x}As_{1-y}P_y$ with $y > 0$ or GaInP as indicated in FIG. 1, and an example for such a device is given in Table II.

TABLE II: Sample description of a strain-balanced quantum well cell with high bandgap barriers.

Layers	Thickness (Å)	Material	Function	Doping	Conc. (cm^{-3})
1	1000	$In_{0.53}Ga_{0.47}As$	Cap	p	1E+19
1	1500	InP	Emitter	p	5E+18
1	50	$Ga_{0.18}In_{0.82}P$	Barrier	i	
49 50	100 100	$Ga_{0.18}In_{0.82}P$ $In_{0.72}Ga_{0.28}As$	Barrier Well	i i	
1	50	$Ga_{0.18}In_{0.82}P$	Barrier	i	
1	5000	InP	Base	n	1E+18
		InP	Substrate	n	

We have developed a model which calculates the SR of multi-layer $In_xGa_{1-x}As_{1-y}P_y$ devices, lattice-matched to InP ($x = 0.47$ y) [M. Paxman et al., J.Appl.Phys.74, 614 (1993), C. Rohr et al., in Thermophotovoltaic Generation of Electricity: Fourth NREL Conf., Vol.460 of AIP Conf. Proc. (American Institute of Physics, Woodbury, New York, 1999), pp.83-92], which has been extended to estimate the SR of strain-balanced $In_xGa_{1-x}As/In_zGa_{1-z}As$ on InP [C. Rohr et al., in Proc. 26th International Symposium on Compound Semiconductors No.166 in Institute of Physics Conference Series (Institute of Physics Publishing, Bristol and Philadelphia, 2000), pp.423-426]. The cell efficiency can be determined given the measured dark current data of the cell, assuming superposition of dark and light current. For photovoltaic applications the p-region of a device would typically be as thin as 1500 Å (instead of 7000 Å) in order to increase the light level that reaches the active i-region where carrier separation is most efficient and to reduce free carrier absorption. A mirror on the back of a semi-insulating (i.e. charge neutral) substrate is particularly useful for QWCs as it

enhances the well contribution significantly. The effect of such a mirror is simulated by doubling the light pass through the wells. The strain-balanced QWC is modelled with these modifications and, for the purpose of comparison, the reflectivity is removed to show the internal quantum efficiency in FIG. 4.

We compare our strain-balanced QWC as well as our lattice-matched InGaAsP QWCs with lattice-matched InGaAs monolithic interconnected modules (MIMs) [N.S. Fatemi et al., in Proc. 26th IEEE PV specialists conf. (IEEE, USA, 1997), pp.799-804], one of the best lattice-matched bulk InGaAs/InP TPV cells, and with bulk GaSb [A.W. Bett et al., in Thermophotovoltaic Generation of Electricity: Third NREL Conf., Vol.401of AIP Conf. Proc. (American Institute of Physics, Woodbury, New York, 1997), pp. 41-53], currently the only material which is being used commercially for TPV applications. To compare efficiencies we assume 'typical' TPV conditions of 100 kW/m^2 normalised power density, grid shading of 5 %, and internal quantum efficiencies for all cells. A back surface reflector is an integral part of MIM technology and particularly useful for QWCs as it enhances the well contribution significantly. It also increases TPV system efficiency because longer wavelength radiation, that is not absorbed by the cell, is reflected back to the source. The efficiency projections for various illuminating spectra are calculated from data presented in FIGs. 3 and 4 and are summarised in Table III. The relative efficiencies are rather more reliable than the absolute values.

TABLE III: Comparison of predicted efficiencies (in %) of bulk InGaAs MIM, GaSb, lattice-matched and strain-balanced quantum well cells with back-mirror using internal quantum efficiencies, under various spectra at 100 kW/m^2, and 5% grid shading:

Spectrum	**Bulk InGaAs MIM**	**Bulk GaSb**	**InGaAsP QWC**	**Strain-bal. QWC**
Solar x 100	16	16	20	19
3200K blackbody	18	18	22	27
2000K blackbody	11	11	12	22
1500K	5.5	5.6	4.8	14

blackbody				
MgO	13	15	16	41
Ytterbia	26	25	42	32
Erbia	37	37	46	43
Holmia	4.5	5.4	4.1	39

The lower dark current of the QWCs (see FIG. 3) is the main reason for their higher efficiencies in Table III. The lattice-matched InGaAsP QWC shows higher efficiencies than the InGaAs MIM and GaSb in all cases except for black-body temperatures below about 2000 K. Higher black-body temperatures, for example 3200 K and the solar spectrum AM1.5 (approximating 5800 K) at 100 times concentration, are favourable for the lattice-matched InGaAsP QWC. Particularly with narrow-band selective emitters such as Ytterbia and Erbia, which are simulated by using narrow-band filters of 950 nm and 1500 nm respectively, the InGaAsP QWC has significant advantages over the InGaAs MIM and GaSb. At black-body temperatures around 2000 K and below, the strain-balanced QWC outperforms the others. Particularly with the MgO emitter, which was designed for a GaSb cell [L. Ferguson and L. Fraas, in Thermophotovoltaic Generation of Electricity: Third NREL Conference Vol.401 of AIP Conf. Proc. (American Institute of Physics, Woodbury, New York, 1997), pp. 169-179], the strain-balanced QWC is significantly better and shows an efficiency which is about 50 % higher than that of a GaSb cell (see Table III).

Based on these results it should be possible to use this concept of strain-balanced QWCs to extend the absorption threshold even further, beyond 2 μm, optimised for TPV applications with a Holmia emitter (see FIG. 5). The efficiency for such a strain-balanced QWC with a Holmia emitter [M.F. Rose et al., Journal of Propulsion and Power 12, 83 (1996)] is predicted to reach 39 % under the same conditions as discussed above. The more the band-edge of a PV cell is extended towards longer wavelengths, the more suitable it becomes for lower temperature sources.

The conversion efficiency can be further substantially increased by reducing the dark current. In strain-balanced devices, this can be achieved if higher band-gap material is used for the barriers as indicated in FIG. 1 and Table II.

We are also developing a model for the dark current behaviour of QWCs. In FIG. 6, a dark current density of an AlGaAs/GaAs quantum well cell is fitted, and it shows that the modelled dark current density for a QWC with a higher band-gap barrier is reduced and hence the efficiency will be increased.

Clauses

1. A semiconductor thermophotovoltaic cell with a p-i-n or n-i-p junction, where a multi-quantum-well system with alternating layers of lower and higher bandgaps is incorporated in the intrinsic region. These layers have also alternating compressive and tensile strain, respectively, with regard to the surrounding material. The strain is compensated by choosing the material compositions and thicknesses of the layers in such a way that the average stress is zero. The number of periods is therefore not limited by strain, and is typically 30-60.

   The material of the barriers is chosen to have a higher than usual bandgap. In the case of a cell based on the InP substrate, the quantum wells are made of $In_xGa_{1-x}As$ material with a composition so that the bandgap is lower than that of the lattice-matched material ($x>0.53$), and the barriers are made of $In_xGa_{1-x}As_{1-y}P_y$ with $y > 0$, in a strain-balanced system as described above.

2. The photovoltaic cell as described in clause 1, where the barriers are made of GaInP.

3. The photovoltaic cell as described in clause 1, where the material of the barriers and/or quantum wells is $Al_xGa_{1-x}As_ySb_{1-y}$, $0 \leq x \leq 1$, $0 \leq y \leq 1$, and the substrate is InP or GaSb.

4. The photovoltaic cell as described in clause 1, where the material of the barriers and/or quantum wells is $In_xGa_{1-x}As_ySb_{1-y}$, $0 \leq x \leq 1$, $0 \leq y \leq 1$, and the substrate is GaSb.

5. The photovoltaic cell as described in clause 1, where the material of the barriers and/or quantum wells is $In_xGa_{1-x}As_{1-y}P_y$, $0 \leq x \leq 1$, $0 \leq y \leq 1$, and the substrate is GaAs.

6. To achieve even lower bandgaps, a virtual substrate (strain-relaxed layer) with a larger lattice-constant is grown, before growing a cell with strain-balanced quantum wells and barriers. This enables one to reach bandgaps that are usually not achievable in that material system and that are necessary for efficient conversion of low temperature sources and particularly for certain narrow band selective emitters such as Holmia.

ABSTRACT
Thermophotovoltaic Device

A photovoltaic cell to convert low energy photons is described, consisting of a p-i-n diode with a strain-balanced multi-quantum-well system incorporated in the intrinsic region. The bandgap of the quantum wells is lower than that of the lattice-matched material, while the barriers have a much higher bandgap. Hence the absorption can be extended to longer wavelengths, while maintaining a low dark current as a result of the higher barriers. This leads to greatly improved conversion efficiencies, particularly for low energy photons from low temperature sources. This can be achieved by strain-balancing the quantum wells and barriers, where each individual layer is below the critical thickness and the strain is compensated by quantum wells and barriers being strained in opposite directions minimising the stress. The absorption can be further extended to longer wavelengths by introducing a strain-relaxed layer (virtual substrate) between the substrate and the active cell.

Drawings

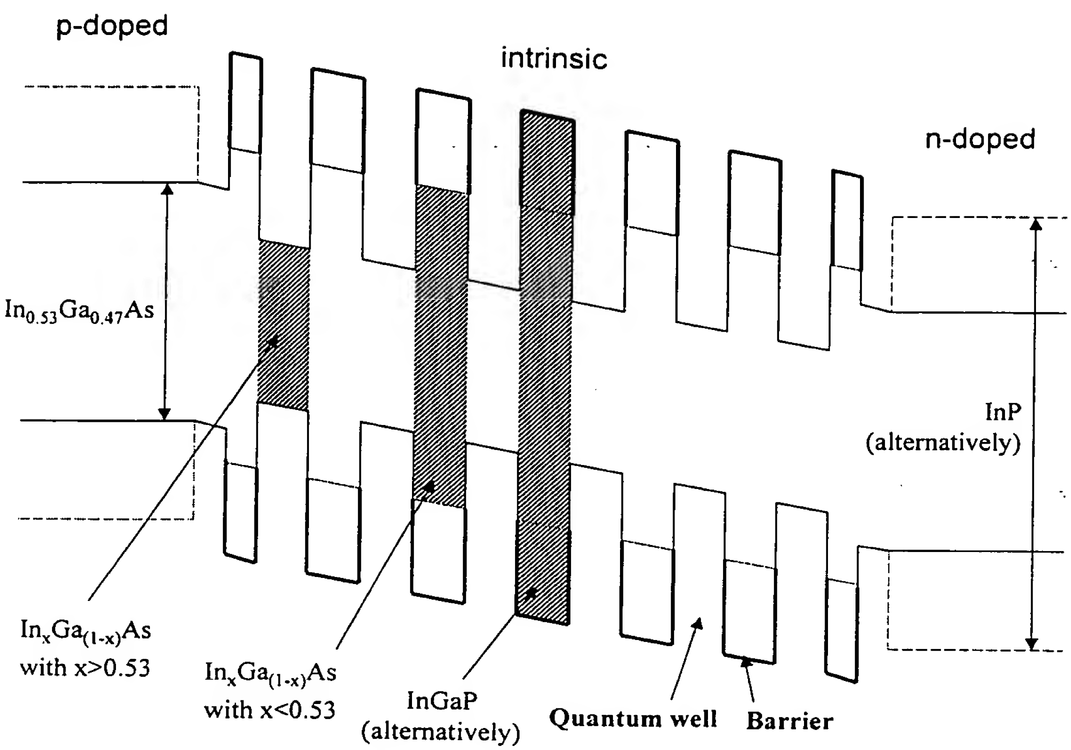

Figure 1: Bandgap diagram of a strain-balanced quantum well cell. The p- and n-regions are made of material that is lattice-matched to the InP substrate, e.g. $In_{0.53}Ga_{0.47}As$ or InP. The quantum wells are made of $In_xGa_{1-x}As$ with $x > 0.53$, and the barrier of $In_xGa_{1-x}As$ with $x < 0.53$, GaInP or InGaAsP.

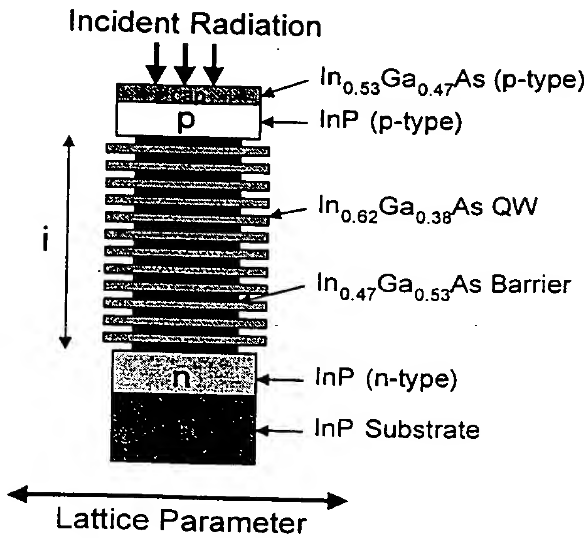

Figure 2: Schematic drawing of a strain-compensated quantum well cell where the width indicates the lattice parameter of the material when unstrained.

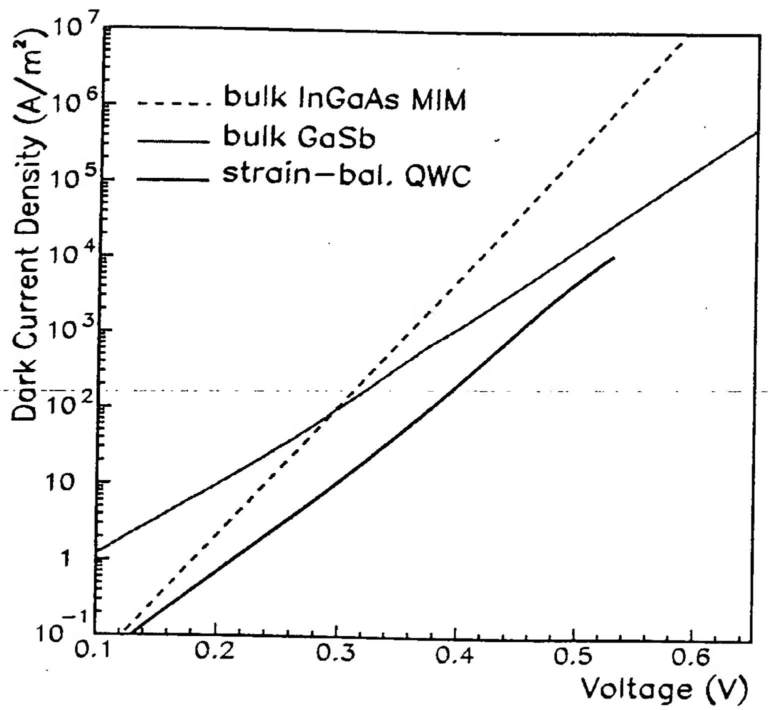

Figure 3: Dark current densities of a strain-balanced quantum well cell (as depicted in Figure 2 but with 30 quantum wells) compared with bulk GaSb of similar effective bandgap (see Figure 4) and lattice-matched bulk InGaAs.

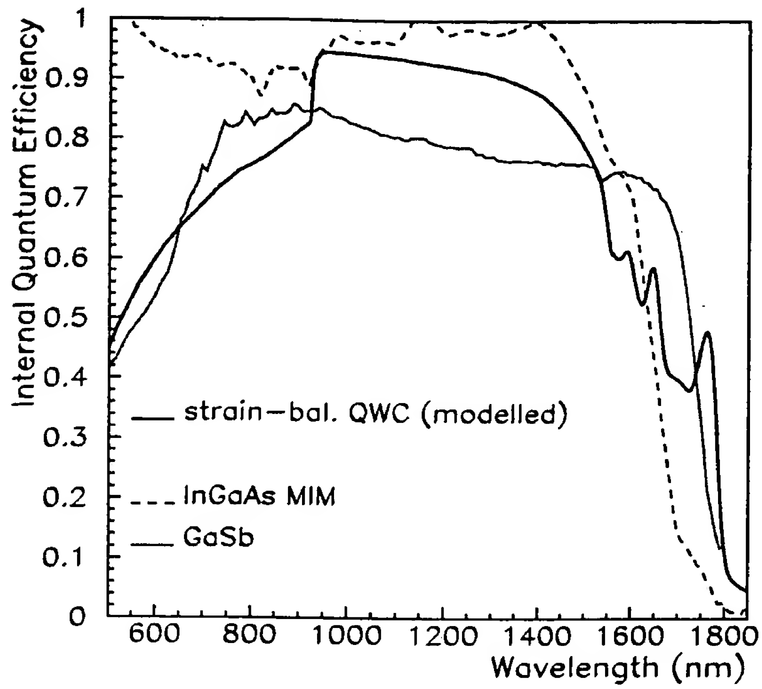

Figure 4: Modelled internal quantum efficiency (with back-surface reflector) of a strain-balanced quantum well cell (as depicted in Figure 2 but with 30 quantum wells) compared with bulk GaSb and lattice-matched bulk InGaAs.

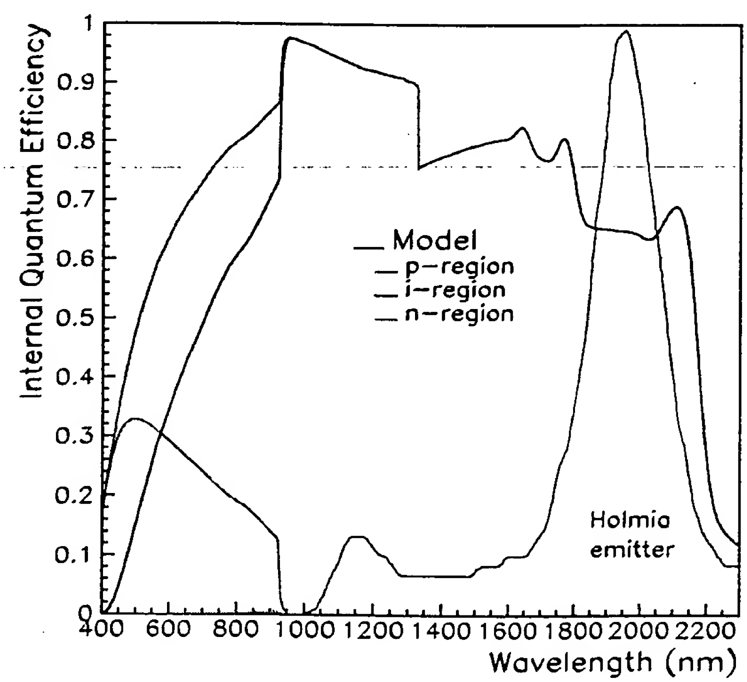

Figure 5: Modelled internal quantum efficiency (with back-surface reflector) of a strain-balanced quantum well cell optimised for a Holmia emitter (not to scale).

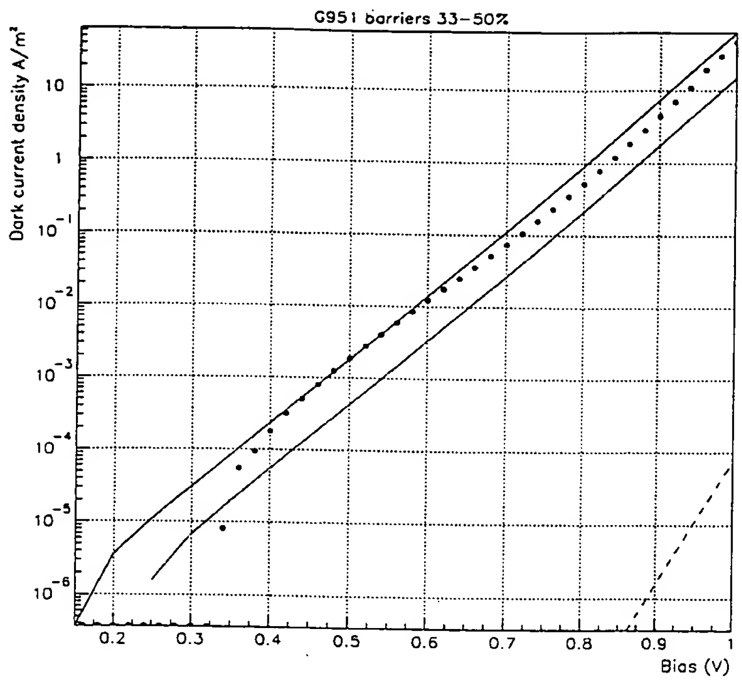

Figure 6: Dark current density of a 50 quantum well AlGaAs/GaAs cell, where the data (dots) is fitted (black line) for 33% Al fraction. The modelled dark current density for a QWC with a higher band-gap barrier of 50% Al (grey line) is reduced.

09/955,297